

BASE MATERIAL FOR LAMINATE, ITS PRODUCTION, PREPREG AND LAMINATED BOARD

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Inventor: KATO YOSHIHISA; ADACHI BUICHI; MURATA
MAMORU
Applicant: OJI PAPER CO LTD
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Abstract of JP11117184

PROBLEM TO BE SOLVED: To obtain an excellent printed circuit board having low warpage by hot-pressing a nonwoven cloth composed of a para-type aramid fiber and a molten liquid crystalline wholly aromatic polyester fiber, impregnating the obtained laminated board substrate with a resin, stacking a plurality of the obtained prepreg sheets and hot-pressing the laminate.

SOLUTION: A wet-formed nonwoven cloth is produced from an aqueous slurry containing 40-95 wt.% of a para-type aramid fiber selected from p-phenylene terephthalamide fiber and p-phenylene diphenyl ether terephthalamide fiber, 5-60 wt.% of a beaten and fibrillated molten liquid crystalline wholly aromatic polyester fiber having an average fiber diameter of 1-5 &mu m, a fiber length of 0.5-3 mm and a melting point of >=300 deg.C and 5-25 wt.% (based on the total weight of the laminated board substrate) of a resin binder. A blended nonwoven cloth produced from the aqueous slurry is hot-pressed with a hot roll under a linear pressure of 120-300 kgf/cm at 190-330 deg.C to obtain a substrate for laminated board. The substrate is impregnated with a thermosetting resin and dried. Plural sheets of the obtained prepreg are laminated and hot-pressed to obtain the objective laminated board.

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(71) Applicant: 000122298
Oji Seishi KK, 5 7-ban 4-chome, Ginza, Chuo-ku,
Tokyo

(72) Inventors: Y. Kato, c/o Nakatsu Works, Oji Seishi KK,
3465-1 Nakatsukawa, Nakatsukawa City, Gifu-ken

T. Adachi, c/o Nakatsu Works, Oji Seishi KK,
3465-1 Nakatsukawa, Nakatsukawa City, Gifu-ken

M. Murata, c/o Nakatsu Works, Oji Seishi KK,
3465-1 Nakatsukawa, Nakatsukawa City, Gifu-ken

(54) [Title of Invention]: SUBSTRATE FOR LAMINATED SHEETS, PROCESS
FOR MANUFACTURE THEREOF, PREPREGS, AND
LAMINATED SHEETS

(57) [Abstract]

[Problem]

To improve on the substrates for laminated sheets made of aromatic polyamide fiber non-woven fabrics with respect to their moisture absorption and warping after having been molded into laminated sheets.

[Means Used to Solve the Problem]

This invention comprises substrates for laminated sheets comprising a mixed paper-made non-woven fabric of para-aramid fibers and a all-aromatic polyester fiber which is liquid crystalline in the melt said fabric being heated to a temperature at which the melt liquid crystalline all-aromatic polyester fiber softens, or higher, in combination with a compression treatment; and a process for manufacture thereof. The use of a melt liquid crystalline all-aromatic polyester fiber with less moisture absorption than that of aromatic polyamide fibers can inhibit the moisture absorption of a substrate or of the laminated sheets themselves. In addition, during the treatment with heat and compression, the softened melt liquid crystalline all-aromatic polyester fibers strongly fuse together or the melt liquid crystalline all-aromatic polyester fibers and para-aramid fibers are strongly fused together, which suppresses any warping after molding into laminated sheets.

[Claims]

[Claim 1]

A substrate for a laminated sheet prepared by a hot-compression treatment of a mixed paper-made non-woven fabric comprised of 40-95% by

weight of para-aramid fibers and 5-60% by weight of all-aromatic polyester fibers which are liquid crystalline in the melt.

[Claim 2]

A substrate for a laminated sheet as set forth in Claim 1 wherein the para-aramid fiber is a type of fibers selected from p-phenylene terephthalamide fibers and p-phenylene diphenyl ether terephthalamide fibers.

[Claim 3]

A substrate for a laminated sheet as set forth in either one of the Claims 1-2 wherein the melt liquid crystalline all-aromatic polyester fibers are fibrillated by a beater into an average fiber diameter of 1-5 μ m and an average fiber length of 0.5-3mm.

[Claim 4]

A substrate for a laminated sheet as set forth in any one of the Claims 1-3 wherein the melt liquid crystalline all-aromatic polyester fiber has a melting point of at least 300°C.

[Claim 5]

A substrate for a laminated sheet as set forth in any one of the Claims 1-4, further comprising a resin binder component, said resin binder being present in the range 5-25% by weight of the total weight of the substrate for laminate sheets.

[Claim 6]

A process for the manufacturing a substrate for a laminated sheet which comprises carrying out a hot-compression treatment of a mixed paper-made non-woven fabric obtained by wet papermaking from an aqueous slurry containing fibers at a ratio of 40-95 parts by weight of para-aramid fibers and 5-60 parts by weight of melt liquid crystalline all-aromatic polyester fibers, using heated rolls at a roll line pressure of 120-300kg f/cm and at a roll temperature in the range of 190-330°C.

[Claim 7]

A process for the manufacture of a substrate for a laminated sheet as set forth in Claim 6 wherein the heated roll hot-compression treatment is carried out twice continuously or discontinuously.

[Claim 8]

A prepreg prepared by impregnating a substrate for a laminated sheet as set forth in any one of the Claims 1-7 with a thermoset resin and drying.

[Claim 9]

A laminated sheet prepared by heat-compression molding a plurality of piled sheets of prepreg as set forth in Claim 8.

[Detailed Description of the Invention]

[0001]

[Technical Field of the Invention]

The present invention relates to a substrate for a laminated sheet made of a mixed paper-made non-woven fabric mainly comprising aromatic polyamide fibers and a process for manufacture thereof. It also relates to prepgs and laminated sheets using the aforesaid substrates for laminated sheets.

[0002]

[Prior Art]

With the recent advance in miniaturization and higher density requirements for electronics, parts mounted to printed wiring boards are being shifted from an insertion type to a surface mounted type so that the mode of mounting on printed wiring boards is also shifting to a surface mounted mode as the mainstream procedure. This mode involves, as a serious problem, the reliability of connections between parts such as the chips which are surface mounted and the printed wiring boards. In other words, it is necessary to bring the coefficients of thermal expansion between the two to be as close to each other as possible. While thin surface mounting type chips have a coefficient of thermal expansion of $5 \times 10^{-6}/^{\circ}\text{C}$, a substrate obtained by impregnating glass non-woven fabric with an epoxy resin will end up having an about 3-fold greater coefficient of thermal expansion.

[0003]

There are also aspects to consider in regard to dielectric constants. In general, the conventional FR-4 has a dielectric constant of about 4.7-5.1; such a relatively high dielectric constant will slow down the rate of propagation of an electrical pulse between adjacent signal circuits resulting in a greatly delayed signal time. In the future the delay time due to signal propagation within a printed wiring board will be an important question so that there will be a need for a low dielectric constant substrate for laminated sheets. Incidentally, FR-4 is a copper clad laminated sheet for a printed wiring board (JIS specification NEMA number) obtained by impregnating a glass substrate with an epoxy resin for lamination.

[0004]

The aforesaid requirements have led to a study of a laminated sheet based on a non-woven fabric substrate comprised of aromatic polyamide fibers that have a negative coefficient of thermal expansion and have a low dielectric constant. A typical example includes Japanese Patent Application Publication H5-65640. The specification describes a substrate prepared by mixed-papermaking from p-phenylene terephthalamide fiber flocks and m-phenylene isophthalamide fibrids, followed by a thermal-compression treatment. However, this substrate exhibits high moisture absorption so that when it is used in a printed wiring board, moisture absorption will cause increases in $\tan\delta$ and the dielectric constant of the substrate as well as electrical problems. There are additional deficiencies in that since it contains no resin binder, a high pressure is required for a compression treatment with hot rolls to reach the desired density, resulting in substantial density variations.

[0005]

Thus, the present inventors studied substrates prepared by mixed-papermaking with drawn p-phenylene diphenyl ether terephthalamide fibers and undrawn m-phenylene isophthalamide fibers, followed by binding between these fibers with a resin binder, followed by a heat-compression treatment. However, the substrate is deficient in that moisture absorption, which can be improved by selecting the fibers, is

still not satisfactory. The adhesion strength attained by a hot compression treatment of undrawn m-phenylene isophthalamide fibrils using hot rolls is inferior to the binding force of m-phenylene isophthalamide fibrils. Therefore, it was discovered that this type of product suffers as a printed wiring board from the deficiency of a large degree of warping on heating.

[0006]

[Problem to be Solved by the Invention]

Therefore, the problem of the present invention to be addressed is to reduce the moisture absorption of a substrate comprised of laminated sheets made of a mixed paper made non-woven fabric mainly based on aromatic polyamide fibers, thereby reducing the moisture absorption of the [resulting] printed wiring board, suppressing a rise in $\tan\delta$ and the dielectric constant, and thus improving on high frequency characteristics, at the same time, suppressing any warping after heating steps with the printed wiring board. This enables one to provide a substrate for laminated sheets having excellent performance as a printed wiring board by taking advantage of the properties possessed by aromatic polyamide fibers.

[0007]

[Means Used to Solve the Problem]

In order to solve the above problems, the present invention employs the following construction. That is, the present invention is constructed from the following Items: (1) - (9) :

(1) A substrate for a laminated sheet prepared by a hot-compression treatment of a mixed paper-made non-woven fabric comprised of 40-95% by weight of para-aramid fibers and 5-60% by weight of all-aromatic polyester fibers which are liquid crystalline in the melt.

(2)

A substrate for a laminated sheet as set forth in(1) wherein the para-aramid fiber is a type of fibers selected from p-phenylene terephthalamide fibers and p-phenylene diphenyl ether terephthalamide fibers.

(3)

A substrate for a laminated sheet as set forth in (1) or (2) wherein the melt liquid crystalline all-aromatic polyester fibers are fibrillated by a beater into an average fiber diameter of 1-5 μm and an average fiber length of 0.5-3mm.

(4)

A substrate for a laminated sheet as set forth in any one of the above (1) - (3) wherein the melt liquid crystalline all-aromatic polyester fiber has a melting point of at least 300°C.

(5)

A substrate for a laminated sheet as set forth in any one of the above (1) - (4), further comprising a resin binder component, said resin binder being present in the range 5-25% by weight of the total weight of the substrate for the laminated sheets.

(6)

A process for manufacturing a substrate for a laminated sheet which comprises carrying out a hot-compression treatment of a mixed paper made a non-woven fabric obtained by wet papermaking from an aqueous slurry containing fibers at a ratio of 40-95 parts by weight of para-aramid fibers and 5-60 parts by weight of melt liquid crystalline all-aromatic polyester fibers, using heated rolls at a roll line pressure of 120-300kg f/cm and at a roll temperature in the range of 190-330°C.

(7)

A process for the manufacture of a substrate for a laminated sheet as set forth in (6) wherein the heated roll hot-compression treatment is carried out twice continuously or discontinuously.

(8)

A prepreg prepared by impregnating a substrate for a laminated sheet as set forth in any one of the above (1)-(7) with a thermoset resin and drying.

(9)

A laminated sheet prepared by heat-compression molding a laminate of a plurality of sheets of prepreg as set forth in the above (8).

[0008]

[Embodiments of the Invention]

In this invention, the term "laminated sheet" means a product obtained by heat compression molding a plurality of preps, including those with metal foil claddings. The term also includes a so-called multi-layer sheets having printed wirings on the interior layer and the surface layer. The term "prepreg" in this invention means a single sheet obtained by impregnating a substrate such as non-woven fabric or the like with a thermoset resin, followed by drying, to be used subsequently in the future for the above laminated sheets. In this invention, a substrate for laminated sheets means a substrate for the above laminated sheets in a state before being impregnated by the resin into a prepreg.

[0009]

The para-aramid fiber used in this invention is an alternating copolymer between an aromatic diamine having para-amino groups and an aromatic dicarboxylic acid having para-carboxyl groups; for example, fibers from poly(p-phenylene terephthalamide), poly(p-phenylene diphenyl ether terephthalamide) and the like. The configurations of the para-aramid fibers are those preferably having a fiber diameter of 5-15 μm and a fiber length of 1-6mm. The finer the fiber diameter of the para-aramid fibers, the more effective in terms of more entanglements in mixed paper made non-woven fabrics in view of the strength of the resultant mixed paper made non-woven fabrics, but generally, a selection is made within above ranges by striking a balance with the slurry dispersion and [the ease of] water filtration during papermaking. With respect to the fiber length of the para-aramid fibers, the longer the fiber, the more effective for generating a greater number of sites for fiber entanglements, and also in view of the strength of the mixed paper made non-woven fabrics, but shorter fiber lengths are better in terms of the slurry dispersion during papermaking, so that a selection is made from the above range.

[0010]

Melt liquid crystalline all-aromatic polyester fibers are those represented by Vektran [which may be misspelled] (trade name of Kuraray Company) obtained by fiber formation from a polyarylate, a copolymer of hydroxy naphthoic acid and hydroxy benzoic acid capable of producing liquid crystals in the melt state, which undergoes a high degree of orientation during spinning to give fibers having super high strength and high heat resistance. The melt liquid crystalline aromatic polyester preferably has a melting point of 300°C or higher. This is because when chip parts are surface mounted on a printed wiring board, heat is applied, which can loosen the adhesion between hot fibers with heat if the melting points of the melt liquid crystalline all-aromatic polyester fiber are low, tending to deform the substrate. The fiber diameter should be 5-20 μm , preferably, 8-18 μm , the fiber length should be about 2-10mm, preferably about 3-6 μm . The manufacture is such that the fiber diameters of 1-5 μm , and fiber lengths about 0.5-3mm are preferred. The finer the fiber diameter for the melt liquid crystalline all-aromatic polyester fiber, the more effective because of greater number of sites for fusing the mixed paper made non-woven fabric in terms of strength of the mixed paper non-woven fabrics, but a selection is made within the above range by a striking a balance between slurry dispersion and the ease of water filtration during papermaking. With respect to the fiber lengths of the melt liquid crystalline or aromatic polyester fibers, the longer the fiber, the more effective because of greater number of fiber fusion sites and in view of the strength of mixed paper made non-woven fabric, but the shorter the fiber length the better in terms of the dispersion of the slurry during papermaking so that a selection is normally made, within the above range.

[0011]

The ratio of the para-aramid fibers and the melt liquid crystalline all-aromatic polyester fibers is 40-95% by weight of para-aramid fibers and 5-60% by weight of all-aromatic polyester fibers. The blend ratio of the melt liquid crystalline all-aromatic polyester fiber should be at least 5% by weight for the fusion of fibers with each other and the reduction of moisture absorption of the substrate for laminated sheets, but not more than 60% by weight in terms of

impregnation by the thermoset resin of the substrate for laminated sheets. The preferred range involves 5-90% by weight of para-aramid fibers and 10-50% by weight of melt liquid crystalline all-aromatic polyester fibers.

[0012]

Having a resin binder in addition to the above two fiber components is also one embodiment of this invention. Addition of a binder permits increasing the bonding strength at a lower heat roll temperature or a lower line pressure at a higher speed. The content of resin binder in the mixed paper-made non-woven fabric should preferably be in the range of 5-25% by weight of the total weight of the non-woven fabrics. A level less than 5% by weight will not give a sufficient effect for improving bond strength by the binder, failing to give the above effect. A level greater than 25% by weight will loosen the adhesion among fibers that constitute the substrate, at the time of molding laminate sheet, so that when the thermoset resin impregnating the substrate melts and flows with heat and pressure at the time of molding the laminate, it will generate the risk of promoting a non-uniform distortion of the substrate; furthermore, during the heat compression treatment with a heat roll, in addition there is the danger of adhering to the heat roll and fuzzing on the surface of said substrate. The resin binders include not only epoxy resins, but also melamine resins, phenolic resins, polyimide resins, polyester resins and the like, to be used in this invention, but not limited to them.

[0013]

An embodiment of a mixed paper-made non-woven fabric in its heat compression stage from a non-woven fabric obtained by wet papermaking from a slurry of para-aramid fiber and an all-aromatic polyester fiber or one containing a resin binder is as follows. The treatment is carried out so as to fuse between the all-aromatic polyester fibers and to fuse the all-aromatic polyester fibers to the para-aramid fibers. Furthermore, this treatment is effective for reducing any voids in the sheet, thereby reducing the amount of impregnating resin required. A large amount of resin creates problems in terms of the resin flow during pressing and an increase in the coefficient in thermal expansion and the like. Carrying out a hot compression treatment by one pass

heat roll treatment enables the manufacture of a substrate, but in terms of variations in the thickness of the substrate material and adhesion to the heat roll and fuzzing of the substrate, it should be carried out in two steps, continuously or discontinuously. By the term "continuous" is meant passing a non-woven fabric from a primary heat roll to a secondary heat roll within 10 plus seconds; the term "discontinuous" means passing through a primary heat roll, followed by once winding up non-woven fabric and then passing the non-woven fabric around a secondary heat roll.

[0014]

If the non-woven fabric contains a binder, it is suitable to set a temperature of 190-250°C with a primary heat roll treatment. The line pressure which is suitable is 120-300Kgf/cm. A heat roll temperature less than 190°C will give insufficient fusion among the all-aromatic polyester fibers or between the aromatic all-aromatic polyester fibers and the para-aramid fibers. At 250°C or higher, the resin binder will adhere to the heat roll to create fuzzing on the substrate surface, which requires attention. In a secondary heat roll treatment, the preferred temperature range is 250-330°C. The preferred line pressure is 120-300Kgf/cm. At 250°C or higher, this will further sufficiently advance the curing of the resin binder with progression of the curing began on curing obtained by the primary heat roll. At a temperature exceeding 330°C, the product will adhere to the heat roll because of the softened melt liquid crystalline all-aromatic polyester fibers, resulting in the danger of generating fibrillation on the substrate surface, which requires attention. There is also the danger of shrinking the substrate. The compression during the primary and secondary heat roll treatment is carried out by applying a line pressure between a pair of heat rolls. When the non-woven fabric passes between the heat rolls, it is necessary for it to receive a designated amount of heat and the speed of movement is preferably not more than 10m/minute, but there is no particular limitation.

[0015]

If no binder is used within the non-woven sheet, that is, in the case of non-woven fabric made of para-aramid fibers and all-aromatic

polyester fibers or fibrils, it is possible to select the temperatures 190°C-330°C for both the primary and secondary heat rolls. A temperature above 330°C will result in the danger of the all-aromatic polyester fiber adhering to the heat rolls. The preferred line pressure is same as the above.

[0016]

The prepgs and laminated sheets using substrates for laminated sheet of this invention are manufactured as below. The substrates obtained by this invention are then impregnated with a thermoset resin such as an impurity-free, high electrical resistance epoxy resin or the like, followed by drying and curing, thereby manufacturing a prepg. Then a plurality of sheets of prepg are compression molded to manufacture laminated sheets. Normally, a metal foil such as copper is clad on top of it to generate a metal clad laminated sheet.

[0017]

[Advantageous Effects of the Invention]

In the substrate for laminated sheets in this invention, the melt liquid crystalline all-aromatic polyester fibers (including the cases where the melt liquid crystalline all-aromatic polyester fibers have been fibrillated) with themselves or the melt liquid crystalline all-aromatic polyester fibers and the para-aramid fibers, are strongly fused together. As a result, even when the thermoset resin which has impregnated the prepgs melts and flows with heat and pressure at the time of molding the laminated sheets, the fusion of the fibers themselves which constitute the substrate is maintained so as to suppress any uneven deformation of the substrate. Similarly, when leadless sheet parts are soldered by a surface mounting mode onto a printed wiring board obtained by fabricating the laminated sheets (metal clad laminated sheets), the substrates are suppressed from a uneven extension or shrinking behavior. Therefore, this will reduce any warping of the laminated sheets. Incorporation of a low moisture absorbing melt liquid crystalline all-aromatic polyester fiber in turn reduces the moisture absorption of the substrate for laminated sheets, reducing the moisture absorption of the printed wiring board, which will suppress any rise in tanδ or dielectric constant due to moisture

absorption, making such a product suitable in high radio frequency applications.

[0018]

[Examples]

<Example 1>

Para-aramid fibers (fiber diameter: 12 μ m; fiber length: 3m, manufactured by Teijin Co., as Technora) and melt liquid crystalline all-aromatic polyester fibers (fiber diameter: 16 μ m; fiber length: 5mm; melting point: 280°C, manufactured by Kuraray as Vectran NT were mixed paper-made, followed by spraying with an aqueous epoxy resin as a resin binder (glass transition temperature 110°C), followed by heating and drying, thereby papermaking a mixed paper-made non-woven fabric of aromatic polyamide fibers and melt liquid crystalline all-aromatic polyester fibers with a unit weight of 72g/m². The contents of the para-aramid fibers, melt liquid crystalline all-aromatic polyester fibers, and the resin binders in the mixed paper manufactured non-woven fabrics are as given in Table 1. Said mixed paper-made non-woven fabric was treated under conditions given in Table 1 (line pressure and roll temperatures) by passing through pairs of primary and secondary heat rolls to heat and compress them so as to soften and fuse together the melt liquid crystalline all-aromatic polyester fibers. The moving speed of the mixed paper made non-woven fabric was set at 10m/min.

[0019]

<Example 2 - Example 7 >

Papers made of non-woven fabrics were prepared by recipes similar to that of Example 1, followed by treating under conditions shown in Table 3 (line pressures and roll temperatures).

[0020]

<Example 8>

Example 1 was repeated for the treatment except for changing the fiber diameter of the para-aramid fiber of Example 1 to 10 μ m.

[0021]

<Example 9>

Example 1 was repeated for the treatment except for changing the fiber length of the para-aramid fiber of Example 1 to 5mm.

[0022]

<Example 10>

Example 1 was repeated for the treatment except for changing the fiber diameter of the melt liquid crystalline all-aromatic polyester fibers of Example 1 to 12 μm .

[0023]

<Example 11>

Example 1 was repeated for the treatment except for changing the fiber length of the melt liquid crystalline all-aromatic polyester fibers of Example 1 to 3mm.

[0024]

<Example 12>

Example 1 was repeated for the treatment except for changing the melt liquid crystalline all-aromatic polyester fibers of Example 1 to a type having a melting point of 308°C (made by Kuraray Co., Vektran HS").

[0025]

<Example 13 - Example 18>

Mixed paper made non-woven fabrics were prepared by the same recipe as that of Example 12 and were treated under conditions given in Table 3 (line pressures and the roll temperatures).

[0026]

<Example 19 - Example 25>

Example 1 was repeated for the treatment except for blending the para-aramid fibers of Example 1 with 2 melt liquid crystalline all-aromatic polyester fibers with different melting points at the contents given in Table 1.

[0027]

<Example 26 - 29 >

Example 1 was repeated for the treatment except for changing the content of the resin binder of Example 1 to that given in Table 1.

[0028]

<Example 30>

Example 1 was repeated for the treatment except for changing the melt liquid crystalline all-aromatic polyester fibers of Example 1 to a fibrillated melt liquid crystalline all-aromatic polyester fiber (average fiber diameter: 2 μm , average fiber length: 1.5mm, melting point: 280°C; manufactured by Kuraray, Vectran NT).

[0029]

<Example 31 - Example 32>

Example 30 was repeated except for changing the content of the fibrillated melt liquid crystalline all-aromatic polyester fibers of Example 30 to those given in Table 1.

[0030]

<Example 33>

Example 30 was repeated for the treatment except for not using any resin binder in papermaking a mixed paper made non-woven fabric.

[0031]

<Comparative Example 1>

Example 1 was repeated for the same recipe treatment except for changing the melt liquid crystalline all-aromatic polyester fibers to meta-aramid fibers (fiber diameter: 16 μm , fiber length: 6mm, manufactured by Teijin; Conex, undrawn).

[0032]

<Comparative Example 2>

Comparative 1 recipe was used for preparing a mixed paper made non-woven fabric which was treated under conditions given in Table 3 (line pressures and roll temperatures).

[0033]

<Comparative Example 3>

Example 1 was repeated for the same treatment except for papermaking a non-woven fabric from the para-aramid fiber and a resin binder.

[0034]

<Comparative Example 4>

Example 1 was repeated for a similar treatment except for changing the content of the melt liquid crystalline all-aromatic polyester fibers of Example 1 to that shown in Table 1.

[0035]

<Comparative Example 5>

Example 12 was repeated for the similar treatment except for changing the content of the melt liquid crystalline all-aromatic polyester fiber of Example 12 to that shown in Table 1.

[0036]

<Comparative Example 6>

Example 30 was repeated except for changing the content of the melt liquid crystalline all-aromatic polyester fiber of Example 30 to that in Table 1.

[0037]

<Fabrication of Laminated Sheets>

The resultant substrate for laminated sheets were impregnated with a brominated bisphenol A-type epoxy varnish to prepare prepgs with a resin pickup of 50% by weight; the prepgs were superposed in a 5-ply layout, along with 18 μ m thick copper foil on both sides to obtain a 0.5mm thick copper clad laminated sheet by hot compression lamination molding. The Technora manufactured by used in these examples was a para-aramid type fiber, a p-phenylene biphenyl ether terephthalamide fiber. Vectran HS and Vectran NT manufactured by Kuraray are those reported to be obtained by solution polymerization of p-hydroxy benzoic acid and 2,6-hydroxy naphthalene carboxylic acid.

[0038]

<Various Evaluations>

(1) The roll dirtying was evaluated at the following levels to be described in Table 3.

Table 3.

● very little ○ little Δ some dirtying ✕ much dirtying

(2) The warping of laminated sheets was evaluated under more stringent conditions than conventional by etching laminated sheets manufactured by the above methods, heat treating for 30 minutes at 150°C, heat treating for 10 minutes at 230°C, and placing the sheet on a flat sheet and making a visual inspection for the warping at edges to give evaluation ratings at the following levels, which were then described in Table 4.

● very low ○ low Δ somewhat high ✕ high

(3) Resin impregnation capability was evaluated at the following levels by visually inspecting the way the resin was impregnated in a substrate at the time of manufacture and the results are described in Table 4.

● very good impregnation ○ good impregnation
Δ somewhat poor impregnation ✕ poor impregnation

(4) Moisture Absorption

The unit weight measurement after allowing a sample to stand 60 days under conditions of 30°C and 80% humidity was defined as post-moisture absorbed unit weight from which percentage was calculated by the following equation (1).

Percent moisture absorption = $100 \times (\text{metric unit weight after moisture absorption} - \text{metric unit weight after absolute drying}) / (\text{metric unit weight after moisture absorption})$ (1)

Incidentally, the column for moisture absorption in Table 4 indicates the moisture absorption of laminated sheets; the substrate moisture absorption column indicates the moisture absorption of substrate before laminated sheets are manufactured.

[0039] [Table 1]

			Substrate Formulation				
					Melt Liquid Crystalline All-aromatic polyester fiber		
	Subst. Unit Wt.	Amount of Binder	p-Aramid Fiber	m-Aramid Fiber	MP 280°C	MP 308°C	Fibrill- ated Mp 280°C
	g/m ²	Wt%/sub- strate	Wt%	Wt%	Wt%	Wt%	WT%
Ex. 1	70	15	80		20		
Ex. 2	70	15	80		20		
Ex. 3	70	15	80		20		
Ex. 4	70	15	80		20		
Ex. 5	70	15	80		20		
Ex. 6	70	15	80		20		
Ex. 7	70	15	80		20		
Ex. 8	70	15	80		20		
Ex. 9	70	15	80		20		
Ex. 10	70	15	80		20		
Ex. 11	70	15	80		20		
Ex. 12	70	15	80			20	
Ex. 13	70	15	30			20	
Ex. 14	70	15	80			20	
Ex. 15	70	15	80			20	
Ex. 16	70	15	80			20	
Ex. 17	70	15	80			20	
Ex. 18	70	15	80			20	
Ex. 19	70	15	90		10		
Ex. 20	70	15	70		30		
Ex. 21	70	15	50		50		
Ex. 22	70	15	50		40	10	
Ex. 23	70	15	50		30	20	
Ex. 24	70	15	50		20	20	
Ex. 25	70	15	50		10	40	
Ex. 26	70	25	80		20		
Ex. 27	70	20	80		20		
Ex. 28	70	10	80		20		
Ex. 29	70	5	80		20		
Ex. 30	70	15	80				20
Ex. 31	70	15	90				10
Ex. 32	70	15	50				50
Ex. 33	70	0	80				20
Com Ex. 1	70	15	80	20			
Com Ex. 2	70	15	80	20			
Com Ex. 3	70	15	100				
Com Ex. 4	70	15	30		70		
Com Ex. 5	70	15	30			70	
Com Ex. 6	70	15	30				70

[0040]

[Table 2]

	Para-aramid fibers		Melt Liquid Crystalline All-Aromatic Polyester Fibers	
	Fiber Diameter μm	Fiber Length mm	Fiber Diameter μm	Fiber Length mm
Ex. 1	12	3	16	5
Ex. 2	12	3	16	5
Ex. 3	12	3	16	5
Ex. 4	12	3	16	5
Ex. 5	12	3	16	5
Ex. 6	12	3	16	5
Ex. 7	12	3	16	5
Ex. 8	10	3	16	5
Ex. 9	12	5	16	5
Ex. 10	12	3	12	5
Ex. 11	12	3	16	3
Ex. 12	12	3	16	5
Ex. 13	12	3	16	5
Ex. 14	12	3	16	5
Ex. 15	12	3	16	5
Ex. 16	12	3	16	5
Ex. 17	12	3	16	5
Ex. 18	12	3	16	5
Ex. 19	12	3	16	5
Ex. 20	12	3	16	5
Ex. 21	12	3	16	5
Ex. 22	12	3	16	5
Ex. 23	12	3	16	5
Ex. 24	12	3	16	5
Ex. 25	12	3	16	5
Ex. 26	12	3	16	5
Ex. 27	12	3	16	5
Ex. 28	12	3	16	5
Ex. 29	12	3	16	5
Ex. 30	12	3	2	1.5
Ex. 31	12	3	2	1.5
Ex. 32	12	3	2	1.5
Ex. 33	12	3	2	1.5
Com Ex. 1	12	3	-	-
Com Ex. 2	12	3		
Com Ex. 3	12	3		
Com Ex. 4	12	3	16	5
Com Ex. 5	12	3	16	5
Com Ex. 6	12	3	2	1.5

[0041] [Table 3]

Roll Temperature		Roll Pressure		Substrate Density	Roll Dirtying
Primary	Secondary	Primary	Secondary	g/cm ³	-
°C	°C	Kg/cm	Kg/cm		
Ex. 1	200	260	180	200	0.55
Ex. 2	240	260	180	200	0.58
Ex. 3	200	320	180	200	0.59
Ex. 4	200	260	250	200	0.57
Ex. 5	200	260	300	200	0.59
Ex. 6	200	260	180	250	0.58
Ex. 7	200	260	180	300	0.58
Ex. 8	200	260	180	200	0.54
Ex. 9	200	260	180	200	0.55
Ex. 10	200	260	180	200	0.54
Ex. 11	200	260	180	200	0.54
Ex. 12	200	260	180	200	0.48
Ex. 13	240	260	180	200	0.52
Ex. 14	200	320	180	200	0.56
Ex. 15	200	260	250	200	0.50
Ex. 16	200	260	300	200	0.53
Ex. 17	200	260	180	250	0.49
Ex. 18	200	260	180	300	0.51
Ex. 19	200	260	180	200	0.45
Ex. 20	200	260	180	200	0.61
Ex. 21	200	260	180	200	0.70
Ex. 22	200	260	180	200	0.68
Ex. 23	200	260	180	200	0.65
Ex. 24	200	260	180	200	0.58
Ex. 25	200	260	180	200	0.56
Ex. 26	200	260	180	200	0.62
Ex. 27	200	260	180	200	0.57
Ex. 28	200	260	180	200	0.52
Ex. 29	200	260	180	200	0.50
Ex. 30	200	260	180	200	0.66
Ex. 31	200	260	180	200	0.55
Ex. 32	200	260	180	200	0.84
Ex. 33	200	260	180	200	0.67
Com Ex 1	200	260	180	200	0.61
Com Ex 2	240	320	200	200	0.65
Com Ex 3	240	320	200	200	0.60
Com Ex 4	200	260	180	200	0.91
Com Ex 5	200	260	180	200	0.82
Com Ex 6	200	260	180	200	1.01

[0042] [Table 4]

Warping of Laminated sheets	Moisture absorption	Resin impregnation	Substrate moisture absorption
-	-	-	-
Ex. 1 ●	0.36	●	1.57
Ex. 2 ●	0.35	●	1.54
Ex. 3 ●	0.35	●	1.52
Ex. 4 ●	0.35	●	1.54
Ex. 5 ●	0.34	●	1.50
Ex. 6 ●	0.35	●	1.52
Ex. 7 ●	0.34	●	1.49
Ex. 8 ●	0.37	●	1.59
Ex. 9 ●	0.36	●	1.57
Ex. 10 ●	0.36	●	1.58
Ex. 11 ●	0.37	●	1.59
Ex. 12 ●	0.38	●	1.63
Ex. 13 ●	0.37	●	1.60
Ex. 14 ●	0.36	●	1.56
Ex. 15 ●	0.37	●	1.61
Ex. 16 ●	0.36	●	1.57
Ex. 17 ●	0.37	●	1.62
Ex. 18 ●	0.37	●	1.60
Ex. 19 ○	0.43	●	1.88
Ex. 20 ●	0.30	●	1.36
Ex. 21 ●	0.20	○	1.02
Ex. 22 ●	0.21	●	1.05
Ex. 23 ●	0.22	●	1.07
Ex. 24 ●	0.23	●	1.10
Ex. 25 ●	0.23	●	1.12
Ex. 26 ○	0.36	●	1.57
Ex. 27 ●	0.35	●	1.55
Ex. 28 ●	0.36	●	1.58
Ex. 29 ●	0.35	●	1.54
Ex. 30 ●	0.35	●	1.54
Ex. 31 ●	0.38	●	1.64
Ex. 32 ●	0.20	○	1.02
Ex. 33 ●	0.35	●	1.55
Com Ex. 1 Δ	0.67	●	2.55
Com Ex. 2 Δ	0.67	●	2.54
Com Ex. 3 xx	0.51	●	1.86
Com Ex. 4 ●	0.14	x	0.80
Com Ex. 5 ●	0.14	Δ	0.79
Com Ex. 6 ●	0.13	x	0.76

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